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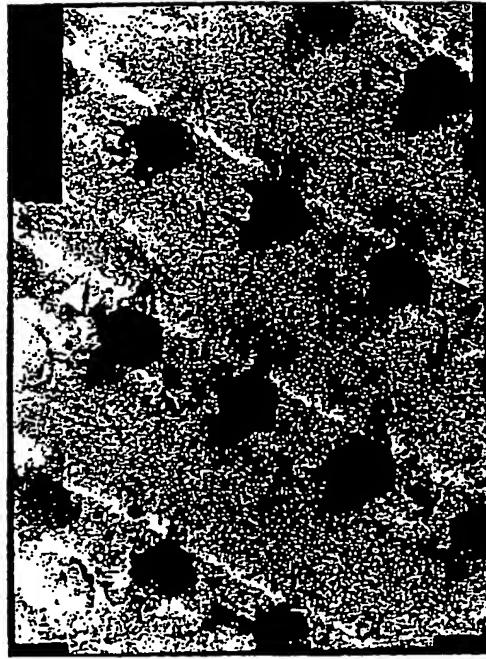
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### (54) Optical recording medium

(57) Formation of small record marks at high shape and dimensional precision is enabled in an optical recording medium of phase change type adapted for formation of small record marks. Thermal stability of such small record marks with high shape and dimensional precision is also improved to provide a highly reliable optical recording medium of phase change type. The optical recording medium of the invention has a recording layer of phase change type, and record marks with minimum length of up to 350 nm are formed in the recording layer. The recording layer contains Ag, In, Sb and Te as its main components. Also provided is an optical recording medium wherein the recording layer also contains Ge and/or N as its sub-component.

FIG. 1



**Description****BACKGROUND OF THE INVENTION****5    Field of the Invention**

[0001] This invention relates to an optical recording medium of phase change type wherein small record marks are formed.

**10    Prior Art**

[0002] Highlight is recently focused on optical recording media capable of recording information at a high density and erasing the recorded information for overwriting. One typical overwritable optical recording medium is phase change optical recording medium wherein a laser beam is directed to the recording layer to change its crystalline state whereupon a change in reflectance by the crystallographic change is detected for reading of the information. The phase change optical recording media are of great interest since the medium can be overwritten by modulating the intensity of a single laser beam and the optical system of the drive unit is simple as compared to magneto-optical recording media.

[0003] Most optical recording media of phase change type used chalcogenide systems such as Ge-Te system and Ge-Sb-Te system which provide a substantial difference in reflectance between crystalline and amorphous states and have a relatively stable amorphous state. It was also recently proposed to use new compounds known as chalcopyrites. Chalcopyrite compounds have been investigated as compound semiconductor materials and have been applied to solar batteries and the like. The chalcopyrite compounds are composed of I<sub>b</sub>-II<sub>b</sub>-VI<sub>b</sub><sub>2</sub> or II<sub>b</sub>-IV<sub>b</sub>-V<sub>b</sub><sub>2</sub> as expressed in terms of the Groups of the Periodic Table and have two stacked diamond structures. The structure of chalcopyrite compounds can be readily determined by X-ray structural analysis and their basic characteristics are described, for example, in Physics, Vol. 8, No. 8 (1987), pp. 441 and Denki Kagaku (Electrochemistry), Vol. 56, No. 4 (1988), pp. 228. Among the chalcopyrite compounds, AgInTe<sub>2</sub> is known to be applicable as a recording material by diluting it with Sb or Bi. The resulting optical recording media are generally operated at a linear velocity of about 7 m/s. See Japanese Patent Application Kokai Nos. (JP-A) 240590/1991, 99884/1991, 82593/1991, 73384/1991, and 151286/1992. In addition to the optical recording media of phase change type wherein chalcopyrite compounds are used, optical recording media of phase change type wherein AgSbTe<sub>2</sub> phase is formed with the crystallization of the recording layer is disclosed in JP-A 267192/1992, 232779/1992, and 166268/1994.

[0004] When information is recorded on the optical recording medium of phase change type, the entire recording layer is first brought into crystalline state, and then, a laser beam of high power (recording power) is applied so that the recording layer is heated to a temperature higher than the melting point. In the region where the recording power is applied, the recording layer is melted and thereafter quenched to form an amorphous record mark. When the record mark is erased, a laser beam of relatively low power (erasing power) is applied so that the recording layer is heated to a temperature higher than the crystallization temperature and lower than the melting temperature. The record mark to which the laser beam of erasing power is applied is heated to a temperature higher than the crystallization temperature and then allowed to slowly cool to recover the crystalline state. Accordingly, in the optical recording media of the phase change type, the medium can be overwritten by modulating the intensity of a single light beam.

[0005] In general, recording density of optical recording media including optical recording media of phase change type can be increased to a level higher than that of magnetic recording media. Today, further increase in the recording density is demanded for processing an enormous amount of information as in the case of image processing. Recording density per unit area can be increased by reducing the record mark length.

[0006] The inventors of the present invention conducted an experiment wherein record marks of different sizes are formed in the recording layer comprising a Ge-Sb-Te-based material which is a common phase change material, and the recording layer is observed by transmission electron microscope. It was then found that coarse crystal grains are formed near the rear end of the record marks, and formation of such coarse crystal grains results in significant deformation of the record marks as well as change in the position of the record mark rear end. The shape of the crystal grains in the rear region of the recorded marks are random, and therefore, the shape of the deformed record marks and the shift of the rear end position differ from mark to mark. The strategy of adjusting the record marks in their reading can not be adopted. When variation in shape and size of the record marks is large in relation to the record mark length, the recording medium will exhibit markedly increased jitter.

[0007] On the bases of such results, the inventors of the present invention have found that critical increase in jitter is induced by the variation in shape and size of the record marks by the formation of coarse crystal grains in the Ge-Sb-Te-based material when the record mark length is reduced to a length below a particular value, more specifically, to 350 nm or less, and in particular to 300 nm or less.

[0008] The inventors of the present invention also found that thermal stability of the record marks formed in the recording layer of phase change type critically reduces when the length of the record mark is reduced beyond the above-specified value, and the resulting recording medium will be less reliable since the record marks are more likely to become crystallized during its storage under high temperature conditions.

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## SUMMARY OF THE INVENTION

[0009] In view of the situation as described above, an object of the present invention is to enable formation of small record marks at high shape and dimensional precision in an optical recording medium of phase change type adapted for formation of small record marks. Another object of the present invention is to improve thermal stability of such small record marks with high shape and dimensional precision to thereby provide a highly reliable optical recording medium of phase change type.

[0010] Such objects are attained by the present invention as described in (1) and (2), below.

- 15 (1) An optical recording medium having a recording layer of phase change type, wherein record marks with minimum length of up to 350 nm are formed in the recording layer, and the recording layer contains Ag, In, Sb and Te as its main components.
- (2) An optical recording medium according to the above (1) wherein the recording layer contains Ge and/or N as its sub-component.

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## BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

- 25 FIG. 1 is a photomicrograph taken by a transmission electron microscope of a recording layer of phase change type containing Ag, In, Sb and Te as its main components. This photograph is presented as a substitute for a diagram showing crystalline structure.
- FIG. 2 is a photomicrograph taken by a transmission electron microscope of a recording layer of phase change type comprising  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . This photograph is presented as a substitute for a diagram showing crystalline structure.
- 30 FIG. 3 is a schematic view showing the record mark.
- FIG. 4 is a schematic view showing an embodiment of the recording pulse strategy.
- FIG. 5 is a cross sectional view of the optical recording medium according to an embodiment of the present invention.
- 35 FIG. 6 is a cross sectional view of the optical recording medium according to another embodiment of the present invention.
- FIG. 7 is a graph showing normalized reflectance of the optical recording medium in relation to the storage period of the medium under high temperature, high humidity conditions.
- FIGS. 8A and 8B are respectively graphs showing normalized reflectance of the optical recording medium in relation to the storage period of the medium under high temperature, high humidity conditions.

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## DETAILED DESCRIPTION OF THE INVENTION

[0012] FIG. 2 is a photomicrograph taken by a transmission electron microscope of a recording layer of phase change type comprising  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  formed by sputtering wherein record marks of 250 nm long are formed. The "record mark length" used herein is the value determined from the linear velocity of the medium and the recording frequency. The dark colored regions regularly appearing in FIG. 2 are the record marks, and the lower left side of the record mark is the rear end. In other words, the record marks are formed by moving the laser beam toward the lower left side of the photograph. In FIG. 2, coarse crystal grains having a diameter almost to reach half of the record mark length are found. The size and number of such coarse crystal grains differ from mark to mark, and it is clear that the record mark length of FIG. 2 greatly vary from mark to mark. The diameter of the coarse crystal grains responsible for such record mark length variation is in the range of from tens to about a hundred nanometers, and therefore, formation of such coarse crystal grains gives considerable influence on the record marks of about 250 nm long.

[0013] FIG. 1 is also an electron photomicrograph of a recording layer of the optical recording medium according to the present invention taken by a transmission electron microscope. This recording layer is the one formed by sputtering, and contains Ag, In, Sb and Te as its main components. The dark colored regions regularly appearing in the recording layer are the record marks as in the case of FIG. 2, and in FIG. 1, the upper left side of the record mark is the rear end. The record mark length in FIG. 1 is the same as that in FIG. 2. In the case of FIG. 1, however, no coarse crystal grains responsible for the record mark deformation are found in contrast to FIG. 2. To be more specific, coarse crystal grains

are present near the rear end of the record marks in FIG. 1 as in the case of FIG. 2. Such coarse crystal grains of FIG. 1, however, hardly affect the rear end shape of the record marks, and variation in the record mark length is minimal.

[0014] As described above, the shape and the size of the record marks are hardly affected by the coarse crystal grains formed near the rear end of the record marks in the recording layer containing Ag, In, Sb and Te as its main components. As a consequence, jitter is minimized to realize accurate reading.

[0015] In the present invention, the recording layer containing Ag, In, Sb and Te as its main components also has Ge and/or N added thereto as its sub-component in order to improve the poor thermal stability of the small record marks as described above. Addition of such sub-component results in the increase of the crystallization temperature as well as the activation energy of the recording layer, and high reliability is thereby realized.

[0016] The present invention is effective when used in an optical recording medium of phase change type wherein small record marks with minimum length of up to 350 nm, and in particular, up to 300 nm are formed. The optical recording medium wherein the present invention is applied is not limited for its method of record mark formation or readout method.

[0017] It should be noted that the serious influence of the coarse crystal grains on the shape and size of the record marks in the Ge-Sb-Te-based recording layer upon formation of the small record marks has not been pointed out. It should also be noted that, although the recording layer containing Ag, In, Sb and Te as its main components has been known in the art, the fact that such recording layer hardly suffers from the problem of the shape and size variation in the small record marks has been utterly unknown.

[0018] Also, importance of the thermal stability of the material constituting the recording layer in the formation of the small record marks of the length shorter than the above-specified value has not been pointed out. Drastic improvement in the thermal stability of such small record marks by the addition of Ge and/or N to the recording layer containing Ag, In, Sb and Te as its main components has also been unknown in the art.

[0019] In the present invention, the record marks are preferably formed such that at least a part of the rear end of the record mark protrudes toward the forward end of the record mark as shown in FIGS. 1 and 2. It should be noted that not all of the record marks are required to have such contour, but at least the minimum record marks should have such contour.

[0020] FIG. 3 is a schematic view showing the record mark. By forming the record mark in such shape, width  $M_w$  of the minimum record mark can be increased beyond the length  $M_L$  of the minimum record mark. It should be noted that  $M_w/M_L$  is preferably at least 1.1. In a recording medium of phase change type, the signal is read as a difference in the reflectance between the amorphous record marks and crystalline regions other than the record marks, and a record mark having a larger width  $M_w$  will result in a higher signal output if the record marks have the same length  $M_L$ . Accordingly, signal output of sufficient level can be attained in the present invention even if the minimum record mark length is reduced to thereby increase the linear recording density. However, an excessively high  $M_w/M_L$  is likely to result in an increased cross erase wherein the record marks on the adjacent track are erased or an increased cross talk wherein the record marks on the adjacent track are read out. In view of such situation, the  $M_w/M_L$  is preferably up to 4, and more preferably up to 3.

[0021] Next, the method adopted to form the record marks having the rear end of the shape as described above, and the reason why the relation  $M_w > M_L$  can be satisfied by the adoption of such method are described.

[0022] As described above, the optical recording medium of phase change type is recorded by irradiating the medium with a laser beam modulated at least between the recording power and the erasing power. When the medium is irradiated by the laser beam at the recording power, the region of the recording layer irradiated by the laser beam melts. The power of the laser beam is maintained for the duration corresponding to the record mark length, and then reduced to the erasing power so that the molten region is rapidly cooled to become amorphous. In the course of the record mark formation as described above, a record mark having the rear end of the shape as described above can be formed by amorphizing not all of the molten region and allowing some of the molten region to be crystallized. To be more specific, the rear end of the record mark is crystallized as shown in FIG. 3 by slowing down the cooling rate of the molten region in its rear end portion (which is the side of the laser beam destination). In the thus formed record marks, it is not likely that all of the rear end protrudes toward the forward end of the record mark, and the record marks typically has the shape as shown in FIG. 3 wherein a tail-like protrusion extending in the direction of the recording track is present at or near the center of the record mark rear end, for example, a shape like a bat with expanded wings.

[0023] Crystallization of some part of the molten region in the formation of the record marks is already described in JP-A 7176/1997. To be more specific, JP-A 7176/1997 describes that recrystallization takes place in the forward end of the record marks when the optical recording disc is operated at a low linear velocity, and suggests that such recrystallization may be prevented by irradiating the medium with a laser beam of recording power level in a pulse train of particular pattern. JP-A 7176/1997 also describes the mechanism of such crystallization. According to JP-A 7176/1997, the heat generated in the region corresponding to the rear half of the record mark by the irradiation of such region with the laser beam is conducted to the region corresponding to the front half of the record mark which has already been melted, and rapid cooling of such region is inhibited to result in the recrystallization of such region. The recrystallization

caused by such mechanism described in the JP-A 7176/1997 is referred to as "self erase" in JP-A 232697/1999.

[0024] As disclosed in the patent documents as described above, it is known that the front end portion of the molten region may crystallize in the course of record mark formation by the "self erase", and that the shape of the front end portion of the record marks is influenced by such crystallization. However, as disclosed in JP-A 7176/1997, emphasis has been laid on the prevention of such influence of self erase on the record mark shape.

[0025] As opposed to such prior art, the rear end of the record marks can be formed in the shape as shown in FIGS. 1 and 2 when the phenomenon similar to such self erase is intentionally induced in the rear end portion of the molten region in order to crystallize the rear end portion of the molten region. The self erase phenomenon may be induced in the rear end portion of the molten region, for example, by controlling the power and duration of the laser beam irradiated to such region. The heat applied by the laser beam irradiated to such region is conducted in the rearward direction, and therefore, cooling rate of the rear end portion of the molten region can be regulated by controlling the power and the duration of the laser beam irradiation, and the length of the crystalline region in the rear end portion of the molten region is simultaneously regulated. When the self erase phenomenon is induced in the rear end portion of the molten region, crystallization mainly takes place in the lengthwise direction of the record mark, and scarcely in the width direction. Accordingly, a record mark having a width relatively longer than its length can be formed by forming a relatively wide record mark having a relatively long length corresponding to its width by the use of a recording power of a relatively high level, and thereafter, crystallizing the rear end portion of the molten region by self erase to thereby form the amorphous record mark of the predetermined length.

[0026] Next, the method employed in practice for regulating the self erase phenomenon in the rear end portion of the molten region is described.

[0027] First, recording pulse strategy is described. An optical recording medium of phase change type is generally recorded, not by continuously irradiating the medium with the laser beam of the recording power for the duration corresponding to the length of the record mark, but by irradiating the medium by with the laser beam divided in a pulse train comprising a plurality of pulses for the control of the record marks as described in JP-A 7176/1997. Constitution of the pulse division is generally referred to as the recording pulse strategy. An embodiment of the recording pulse strategy is shown in FIG. 4 wherein a typical recording pulse train corresponding to 5T signal of NRZI signal is illustrated. In FIG. 4,  $T_{top}$  represents width of the top pulse,  $T_{mp}$  represents width of the pulses other than the top pulse (which are also referred to as multi-pulse), and  $T_{cl}$  represents width of the downward pulse (also referred to as the cooling pulse) after the last pulse. Such pulse width is generally indicated by the value normalized with standard clock width (1T). In the recording pulse strategy shown in FIG. 4, power (bias power  $P_b$ ) of all of the downward pulses including the cooling pulse is set at a value lower than the erasing power  $P_e$ .

[0028] When the power of the laser beam is modulated by the recording pulse strategy as described above, the self erase phenomenon in the rear end portion of the molten region can be regulated by controlling at least one of the recording power  $P_w$ ,  $T_{mp}$ , power of the cooling power (bias power  $P_b$  in the illustrated embodiment),  $T_{cl}$  and the erasing power  $P_e$ . Although the control scheme may be adequately selected depending on the composition of the recording layer, the structure of the medium, and other factors relevant to the crystallization of the molten region, it is generally preferable to regulate at least one of the recording power  $P_w$ , the erasing power  $P_e$ , and  $T_{cl}$ .

[0029] Such regulation of the record mark length by the use of the self erase phenomenon results in the increased flexibility in setting the record mark width. For example, a wide record mark of the predetermined length can be formed by increasing both the recording power and the power after irradiating the record power (cooling pulse power and/or erasing power), namely, by melting a large area and increasing the area crystallized within the rear end portion of the molten area; while a narrow record mark of the predetermined length can be formed by reducing both the recording power and the power after irradiating the record power, namely by melting a small area and reducing the area crystallized within the rear end portion of the molten area. Therefore, a fully wide record mark extending beyond the recording track can be formed when either one of the guiding groove and the land between two adjacent guide grooves is used for the recording track, while a considerably wide track without extending beyond the recording track can be formed in the case of the land/groove recording wherein both the groove and the land are used for the recording tracks. A high signal output is thereby realized in both cases.

[0030] As described above, when the self erase phenomenon is used by adequately changing the power of the laser beam after irradiating the recording power, formation of the record mark of the same length is enabled even if the recording power was changed. In other words, utilization of the self erase phenomenon has enabled to increase flexibility in selecting the range of the recording power (recording power margin) for forming the record marks of predetermined length.

[0031] In contrast, when the self erase phenomenon is not utilized for the formation of the rear end of the record marks, the rear end of the record marks formed will have a rounded shape like the front end of the record mark as shown in FIG. 2 of JP-A 7176/1997. When the length of the record mark is reduced in such a case, width of the record mark will be reduced simultaneously with the record mark length, and the area of the record mark will be insufficient to attain sufficient output. In addition, when the self erase phenomenon is not utilized, the record mark length will be sub-

stantially determined solely by the recording power and the recording power margin will be reduced.

[0032] Furthermore, jitter will be reduced by the use of the self erase phenomenon in the formation of the rear end of the record marks when compared to the case wherein circular or oblong record marks are formed. Such effect is particularly remarkable in the formation of the minimum record mark. Even if the record mark had a sufficient width, circular and oblong record marks suffer from increased jitter compared to the case wherein the self erase phenomenon is utilized in the formation of the rear end of the record marks. It is generally taken for granted in the art that a record mark with a highly symmetric contour with no indentation or protrusion results in the reduced jitter. It is the inventors of the present invention who have for the first time found that the jitter can be reduced by adopting the record mark of highly asymmetrical shape.

[0033] Use of the self erase enables increase in the record mark width in relation to the record mark length, and hence, decrease in the signal output by the decrease in the record mark length is suppressed. Therefore, use of the self erase is particularly effective when decrease in the minimum record mark length is required, and to be more precise, when the relation:

$$M_L \leq 0.4\lambda/NA$$

is required when  $M_L$  is the minimum record mark length,  $\lambda$  is the wavelength of the recording laser beam, and NA is the numerical aperture of the objective lens of the recording optical system. When the small record marks are formed without utilizing the self erase in the rear end portion of the molten region, the record marks formed will be circular or semi-circular, and the record mark width will be reduced to the extent equivalent to the record mark length, and the signal output will be accordingly reduced. The inventors of the present invention have found that the signal output is reduced beyond the critical level when the relation:  $M_L \leq 0.4\lambda/NA$  is met. In contrast, when the self erase is utilized for the formation of the record marks, the record mark width can be increased in relation to the record mark length, and record marks with sufficient width can be formed even if the relation:  $M_L \leq 0.4\lambda/NA$  is met and signal output of sufficient level can be thereby obtained.

[0034] The coarse crystal grains near the rear end of the record marks in FIGS. 1 and 2 are those formed by crystallization of the rear end portion of the molten region. The small variation in the record mark length of FIG. 1 is believed to have been realized by the situation that, in the recording layer containing Ag, In, Sb and Te as its main components, crystallization occurs depending on the cooling rate distribution in the rear end portion of the molten region, and the crystallization terminates at the position where the cooling rate reaches the critical value for crystallization. In contrast, the large variation in the record mark length of FIG. 2 is believed to have been induced by the situation that crystallization in the recording layer of  $Ge_2Sb_2Te_5$  proceeds and terminates beyond and before the position where the cooling rate reaches the critical value for crystallization once the crystallization has started in the region cooled at a slow rate.

[0035] It should be noted that the optical recording medium of the present invention can be used in the recording other than the recording wherein the self erase phenomenon near the rear end portion of the molten region is utilized. To be more precise, the benefit of the use of the recording layer containing Ag, In, Sb and Te as its main components can be realized in every recording method wherein the record mark length is regulated by crystallizing a part of the molten region.

[0036] Also, the benefit of improving the thermal stability of the small record marks is realized even if the self erase phenomenon is not utilized.

[0037] The phase change type recording layer of the optical recording medium according to the present invention contains Ag, In, Sb and Te as the main components, and Ge and/or N as the sub-component. When the atomic ratio of the main components is represented by the formula (I):



a, b, c, and d are preferably in the range of:  $0.02 \leq a \leq 0.20$ ,  $0.02 \leq b \leq 0.20$ ,  $0.35 \leq c \leq 0.80$ , and  $0.08 \leq d \leq 0.40$ ; and more preferably, in the range of:  $0.02 \leq a \leq 0.10$ ,  $0.02 \leq b \leq 0.10$ ,  $0.50 \leq c \leq 0.75$ , and  $0.10 \leq d \leq 0.35$ .

[0038] If the value of a is too small in formula (I), recrystallization of the record marks, and hence, repetitive overwriting will become difficult. In contrast, if the value of a is too large, excess silver will solely diffuse into the antimony phase during the recording and erasure. This results in a reduced rewriting durability, less stability of both the record marks and the crystalline regions, and loss of reliability. Specifically, when the medium is stored at an elevated temperature, crystallization of the record marks will be promoted to invite drops of C/N and degree of modulation. In addition, the medium will undergo faster degradation in C/N and modulation degree in the repeated recording operations.

[0039] If the value of b is too small in formula (I), the record marks will become less amorphous to result in reduced degree of modulation and insufficient reliability. If the value of b is too large, reflectance of the regions other than the record marks will become reduced and the degree of modulation will be reduced.

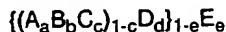
[0040] If the value of c is too small in formula (I), difference in the reflectance created by the phase change will be

sufficient, but erasure will be difficult due to markedly reduced rate of crystal transition. If the value of c is too large, the reflectance difference created by the phase change will be insufficient to invite drop in the degree of modulation.

[0041] If the value of d is too small, the recording layer will be difficult to render amorphous, and signal recording may become impossible. If the value of d is too large, crystal transition rate will be excessively low to render the erasure difficult.

[0042] Content of the germanium in the recording layer is preferably up to 25 at%, and more preferably up to 15 at%. When the germanium content is too high, properties of the Ag-In-Sb-Te-based recording material will not be fully realized. Germanium is preferably added in an amount of at least 1 at%, and more preferably in an amount of at least 2 at% in order to fully improve the stability in reading by the germanium addition.

[0043] JP-A 267926/1996 discloses an optical recording medium having a recording layer of phase change type represented by the formula:



wherein A is Ag and/or Au; B is Sb and/or Bi; C is Te and/or Se; D is In, or In and Al and/or P; and E is at least one element selected from Si, Ge, Sn, and Pb; and a, b, c, d, and e represent atomic ratio such that:

$$0.001 \leq a \leq 0.20,$$

20                    $0.40 \leq b \leq 0.90,$

$$0.10 \leq c \leq 0.50,$$

$$a + b + c = 1,$$

25                    $0 < d \leq 0.06$ , and

$$0.001 \leq e \leq 0.10.$$

30 The recording layer of phase change type described in JP-A 267926/1996 and the optical recording medium of the present invention share the common features of including Ag, In, Sb and Te as the main components and the possibility of including Ge. The invention described in JP-A 267926/1996, however, attempts to realize a sufficient degree of erasure even when the medium is operated at a high linear velocity by the addition of element E which may be Ge, and this invention is different in this respect from the present invention. JP-A 267926/1996 is also silent about the critical improvement in the thermal stability of the small record marks of the length of up to 350 nm realized by the addition of Ge. As described in the Examples of the present invention, the thermal stability of the small record marks undergo a specific improvement by the addition of Ge. In contrast, the elements mentioned in JP-A 267926/1996 as being equivalent to Ge do not have the merit of improving the thermal stability of the small record marks.

[0044] Nitrogen may be introduced in the recording layer, for example, by conducting the sputtering of the recording layer in an atmosphere containing nitrogen in addition to the rare gas such as argon. Flow rate ratio of the atmospheric gas (nitrogen gas/rare gas) may be adjusted so that benefits of nitrogen addition is sufficiently realized while avoiding excessive introduction of the nitrogen gas. The ratio is preferably in the range of 2/150 to 8/150. When the flow rate ratio is too low, nitrogen content in the recording layer will be insufficient to realize the benefits of the nitrogen addition. In contrast, when the flow rate ratio is too high, nitrogen content in the recording layer will be too high and the reflectance difference created by the phase change will be reduced to result in the insufficient degree of modulation.

[0045] The recording layer may optionally contain elements other than the main components and the sub-components as described above. Such additional elements may be element M which is at least one element selected from H, Si, C, V, W, Ta, Zn, Ti, Ce, Tb, Sn, Pb and Y. The element M is effective for improving rewriting durability, and more specifically, for preventing loss of erasability as a result of repetitive rewriting operations. Of the elements as mentioned above, inclusion of at least one member selected from V, Ta, Ce, and Y is preferred because the effects are more outstanding. Content of the element M in the recording layer is preferably up to 10 at%. When the content of the element M is too high, the reflectance difference created by the phase change will be reduced to invite insufficient degree of modulation.

[0046] The recording layer preferably consists essentially of the elements as described above. However, it is acceptable that Ag is partially replaced by Au; Sb is partially replaced by Bi; Te is partially replaced by Se; and In is partially replaced by Al and/or P.

[0047] The percent replacement of Ag by Au is preferably up to 50 at%, and more preferably up to 20 at%. When the percent replacement is too high, the record marks are likely to crystallize, and loss of reliability at elevated temper-

ature is invited.

[0048] The percent replacement of Sb by Bi is preferably up to 50 at%, and more preferably up to 20 at%. When the percent replacement is too high, the recording layer will have an increased absorption coefficient, and the optical interference effect will be reduced. This results in reduced difference in reflectance between the crystalline region and the amorphous region, and hence, in reduced degree of modulation as well as in the difficulty of realizing a high C/N.

[0049] The percent replacement of Te by Se is preferably up to 50 at%, and more preferably up to 20 at%. When the percent replacement is too high, crystal transition rate will be too slow and the erasability will be insufficient.

[0050] The percent replacement of In by Al and/or P is preferably up to 40 at%, and more preferably up to 20 at%.

When the percent replacement is too high; record marks will become less stable to result in the loss of reliability. The proportion of Al and P is arbitrary.

[0051] The recording layer is preferably formed to a thickness of 9.5 to 50 nm, and more preferably, to a thickness of 13 to 30 nm. When the recording layer is too thin, growth of the crystalline phase will be difficult and the reflectance difference created by the phase change will be insufficient. When the recording layer is too thick, the recording layer will have an increased heat capacity to render the recording difficult. An excessively thick recording layer also results in the reduced reflectance and in the reduced degree of modulation.

[0052] The composition of the recording layer may be identified by electron probe microanalysis (EPMA), X-ray microanalysis, ICP, etc.

[0053] The recording layer is preferably formed by sputtering. The sputtering conditions are not particularly limited. For example, when a recording layer comprising a material including two or more elements are to be formed, the sputtering may be conducted by using an alloy target, or alternatively, by multi-target sputtering wherein two or more targets are used.

[0054] In the present invention, the optical recording medium is limited only by the composition of the recording layer and the dimension of the record marks, and optical recording media of non-limited structure may be employed as long as such features are satisfied.

[0055] A typical embodiment of the optical recording medium of phase change type comprises a substrate 2; and a first dielectric layer 31, a recording layer 4, a second dielectric layer 32, a reflective layer 5, and a protective layer 6 disposed on the substrate 2 in this order. In the medium of such embodiment, the recording/reading light is irradiated through the substrate 2.

[0056] The optical recording medium of the present invention may also have a constitution shown in FIG. 6. In the case of such constitution, the reading laser beam is irradiated without passing through the substrate 2, and in this case, the reflective layer 5, the second dielectric layer 32, the recording layer 4, the first dielectric layer 31, and the protective layer 6 are stack on the substrate 2 in this order.

[0057] The present invention is applicable not only to the rewritable optical recording medium of phase change type but also to the write-once type optical recording medium of phase change type. The write-once type medium is a recordable medium wherein the once formed record marks are unerasable. The term "unerasability" used herein does not mean that the medium is unerasable under all conditions but that the medium is recordable but unerasable (namely, the record marks are uncyclizable) when the medium is subjected to an overwriting operation under the conditions the same as those of the rewritable medium (namely, at the same erasing power and the linear velocity). Such write-once type medium can be realized by forming the recording layer from a composition which is difficult to crystallize, for example, from a composition having a high crystallization temperature. Ordinary rewritable medium can be used as a write-once type medium by reducing the erasing power and/or by increasing the linear velocity of the medium.

## EXAMPLES

[0058] Examples of the present invention are given below by way of illustration and not by way of limitation.

### Example 1

[0059] Samples for evaluation were prepared by using a slide glass for the substrate 2, and forming a first dielectric layer, a recording layer, a second dielectric layer, and a reflective layer on the substrate 2 in this order.

[0060] The first dielectric layer was formed by sputtering in argon atmosphere using ZnS (80 mol%) - SiO<sub>2</sub> (20 mol%) for the target. The first dielectric layer was formed to a thickness of 80 nm.

[0061] The recording layer formed was the one containing the components as shown in Table 1 for the main components and the sub-components. The recording layer was prepared by sputtering in argon atmosphere or argon and nitrogen (N<sub>2</sub> + Ar) atmosphere (in the case of nitrogen introduction) using Ag-In-Sb-Te alloy or Ag-In-Sb-Te-Ge alloy for the target. The atomic ratio of the main components was:

$$a = 0.07,$$

b = 0.05,  
 c = 0.59, and  
 d = 0.29

- 5 in formula (I):  $\text{Ag}_a\text{In}_b\text{Sb}_c\text{Te}_d$ . The recording layer was formed to a thickness of 23 nm. Ge content of the recording layer is shown in Table 1. Flow rate ratio of the atmospheric gas ( $\text{N}_2/\text{Ar}$ ) in the formation of the recording layer is also shown in Table 1.

[0062] The second dielectric layer was formed by sputtering in argon atmosphere using  $\text{ZnS}$  (50 mol%) -  $\text{SiO}_2$  (50 mol%) for the target. The second dielectric layer was formed to a thickness of 25 nm.

- 10 [0063] The reflective layer was formed by sputtering in argon atmosphere using Al - 1.7 at% Cr for the target. The reflective layer was formed to a thickness of 100 nm.

#### Evaluation

- 15 [0064] Crystallization temperature of the recording layer 4 was determined by placing the sample on a heating stage, irradiating the sample with the laser beam through the substrate 2 as the temperature is elevated at 30°C/min, and measuring the temperature of the reflectance change. The samples were also evaluated for increase in activation energy by the addition of Ge to the Ag-In-Sb-Te layer through measurement of the activation energy of the recording layer by Arrhenius method. The results are shown in Table 1.

20

Table 1

Sample No.	Main Components	Sub-Component	Ge content (at %)	$\text{N}_2/\text{Ar}$	Crystallization temp. (°C)	Activation energy (eV)
1	Ag-In-Sb-Te	-	-	-	175.5	3.15
2	Ag-In-Sb-Te	Ge	2	-	185	3.41
3	Ag-In-Sb-Te	Ge	5	-	201	4.59
4	Ag-In-Sb-Te	Ge	10	-	231	4.95
5	Ag-In-Sb-Te	N	-	5/150	193.5	-
6	Ag-In-Sb-Te	N	-	10/150	207	-

105 105

- 35 [0065] As shown in Table 1, addition of Ge or N as the sub-component results in the increase of crystallization temperature, and addition of Ge as the sub-component is also associated with the increase in the activation energy.

- [0066] It should be noted that the reflectance difference (difference between the reflectance in crystalline state and the reflectance in amorphous state) was 3.6% when the recording layer was formed in the atmosphere free from  $\text{N}_2$ , 40 while the reflectance difference was 3.1% at  $\text{N}_2/\text{Ar}$  of 5/150 and 2.3% at  $\text{N}_2/\text{Ar}$  of 10/150. It was thus confirmed that addition of N to the recording layer results in the decrease of modulation degree.

#### Example 2

- 45 [0067] A substrate 2 in the form of a disc having a diameter of 120 mm and a thickness of 0.6 mm was prepared by injection molding polycarbonate. Grooves were simultaneously formed in the injection molding of the substrate 2. On the grooved surface of the substrate 2, there were formed a first dielectric layer, a recording layer, a second dielectric layer, and a reflective layer in this order by the procedure as described for the evaluation sample Nos. 1 to 6 in Example 1 to produce optical recording disk sample Nos. 1 to 6.

- 50 [0068] The recording layer of the thus produced sample was initialized (crystallized) by a bulk eraser and the sample was placed on an optical recording medium evaluator. The sample was overwritten under the conditions as described below:

Laser beam wavelength: 638 nm

55 Numerical aperture, NA: 0.6

Linear velocity: 3.5 m/s

Recorded signal: single signal corresponding to the record mark length of 250 nm. The recording pulse strategy was of the pattern shown in FIG. 4 wherein:

$$T_{top} : T_{mp} : T_{cl} = 0.5 : 0.3 : 0.5,$$

Number of multipath = 1,

$P_w = 11.0 \text{ mW}$ ,

$P_e = 5.0 \text{ mW}$ ,

$P_b = 0.5 \text{ mW}$ .

The sample was then stored in the environment of  $80^\circ\text{C}$  and 80% RH for 100 hours.

[0069] Average reflectance of the track formed with the record marks was measured before and after the storage to find the alteration in the reflectance. If the record marks crystallize during the high temperature storage, the average reflectance will be altered. For comparison purpose, a medium recorded with the single signal corresponding to the record mark length of 620 nm was measured for the reflectance in the same manner except that reflectance at the record mark and not the average reflectance of the track was measured in the case of the record mark length of 620 nm. At the record mark of 620 nm, reflectance alteration was found in no sample while reflectance alteration was noted in Sample No. 1 having the sub-component-free recording layer when the record mark length was 250 nm.

[0070] When the record mark length was reduced to 150 nm, and the samples were measured after storing at  $80^\circ\text{C}$  and 80% RH, Sample No. 1 exhibited reflectance alteration after storing for 50 hours while other samples exhibited no reflectance alteration after storing for 100 hours.

[0071] A photomicrograph of Sample No. 2 after forming the record marks of 250 nm long taken by a transmission electron microscope is shown in FIG. 1. A photomicrograph was also taken by a transmission electron microscope for a sample having the record marks of 250 nm long formed thereon which had been prepared as in the case of the above-described samples except that the composition of the recording layer was  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , and the photomicrograph is shown in FIG. 2. It should also be noted that, in the sample shown in FIG. 2, the recording pulse strategy was such that:

$$T_{top} : T_{mp} : T_{cl} = 0.5 : 0.22 : 0.5$$

and other recording conditions were the same as those of the sample of FIG. 1

[0072] Comparison of FIG. 1 with FIG. 2 revealed that the record marks are less deformed in the Ag-In-Sb-Te-based recording layer. As in the case of FIG. 1, the contour of the record mark rear end was not greatly affected by the coarse crystal grains in the Sample Nos. 1 and 3 to 6 shown in Table 1.

[0073] It should be noted that  $M_w/M_L$  was 1.8 or more in FIG. 1, and 2.2 or more in FIG. 2.

### Example 3

[0074] Sample No. 3 produced in Example 2 was formed with record marks of 300 nm long by repeating 10 over-writing operations, and the recorded sample was stored under high temperature, high humidity conditions of  $80^\circ\text{C}$  and 80% RH to evaluate the relation between the reflectance and the storage period. It should be noted that the reflectance measured was the reflectance at the record mark. For comparison purpose, samples having a recording layer containing the elements mentioned as being equivalent to Ge (namely, Si or Sn) in JP-A 267926/1996 were also produced, and these samples were also evaluated for the relation between the reflectance and the storage period. The results are shown in FIG. 7. The "normalized reflectance" in the vertical axis of FIG. 7 is the reflectance normalized by the reflectance before the storage.

[0075] As demonstrated in FIG. 7, the recording layer having the elements other than Ge added thereto exhibited a steep increase in the reflectance before storing for 300 hours to indicate the crystallization of the record marks. In contrast, no substantial increase in the reflectance was noted after passing 1000 hours when the recording layer had Ge added thereto. The advantageous effects of Ge addition for the improvement in the stability of small record marks was clearly demonstrated by such results.

[0076] Next, a sample was prepared as in the case of the Sample No. 3 except that the main composition of the recording layer was changed in the formula (I):  $\text{Ag}_a\text{In}_b\text{Sb}_c\text{Te}_d$  such that

$a = 0.06$ ,

$b = 0.04$ ,

$c = 0.62$ , and

$d = 0.28$ , and

the amount of the Ge added to the recording layer was varied in the range of from 0 to 2 at%. The samples were formed with the record marks of 300 nm long, and evaluated by storing under high temperature, high humidity conditions as in

the case of foregoing Examples. The results are shown in FIGS. 8A and 8B. FIG. 8A shows the results for the case wherein the sample was recorded only once after the initialization of the recording layer. FIG. 8B shows the results for the case wherein the samples were subjected to 1000 overwriting operations after the initialization. The amount of the Ge added is indicated in the figures.

5 [0077] As demonstrated in FIG. 8A, increase in the reflectance during the storage is significantly suppressed by the addition of Ge. In particular, no substantial increase in the reflectance was noted when Ge was added at an amount of 1 at% or more. FIG. 8B demonstrates that no substantial increase in the reflectance is noted when the Ge was added in an amount of 2 at% even when the medium was subjected to 1000 overwriting operations and stored for 200 hours.

10 BENEFITS OF THE INVENTION

[0078] The present invention has enabled to form small record marks with stable shape and size in the optical recording medium of phase change type. The present invention has also enabled to improve thermal stability of the small record marks.

15 [0079] Japanese Patent Application No. 368539/1998 is incorporated herein by reference.

[0080] Although some preferred embodiments have been described, many modifications and variations may be made thereto in the light of the above teachings. It is therefore to be understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

20 **Claims**

1. An optical recording medium having a recording layer of phase change type, wherein record marks with minimum length of up to 350 nm are formed in the recording layer, and the recording layer contains Ag, In, Sb and Te as its main components.
- 25 2. An optical recording medium according to claim 1 wherein the recording layer contains Ge and/or N as its sub-component.

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35

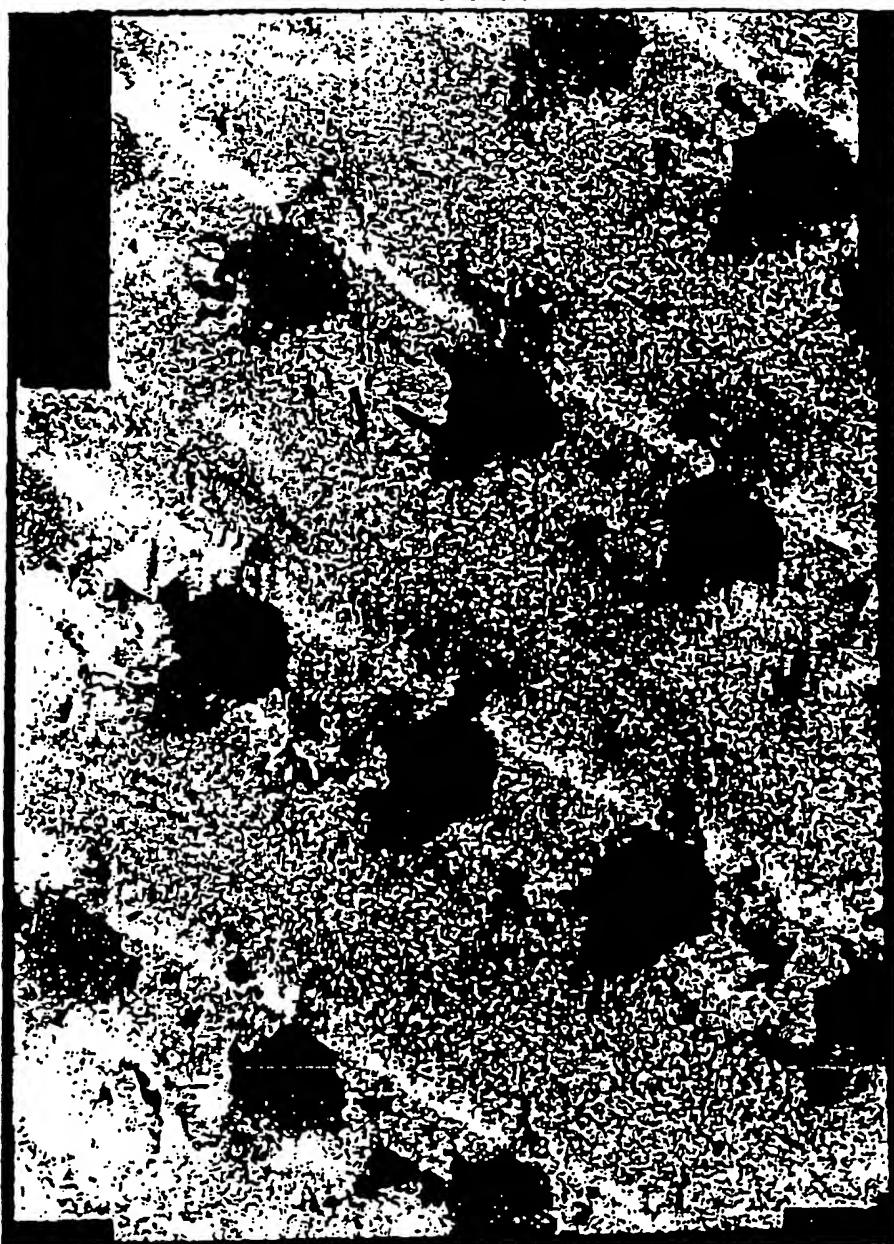
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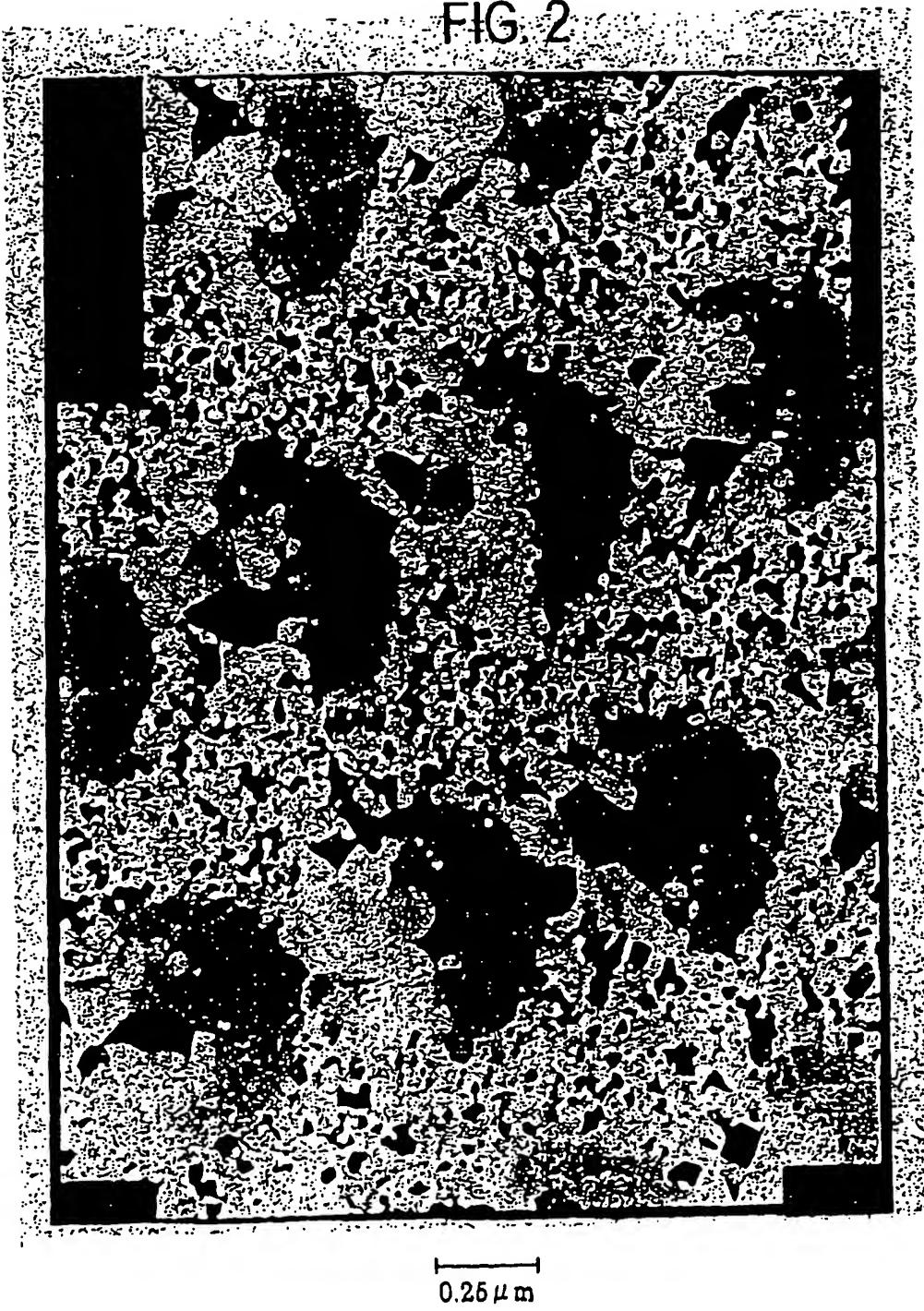
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FIG. 1



0.25  $\mu$ m

FIG. 2



0.25  $\mu$ m

FIG. 3

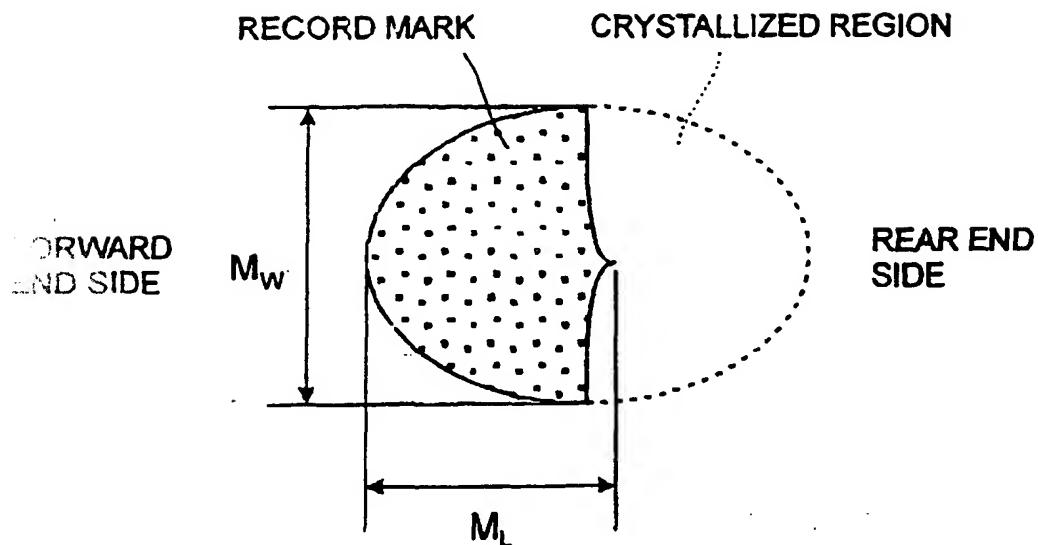
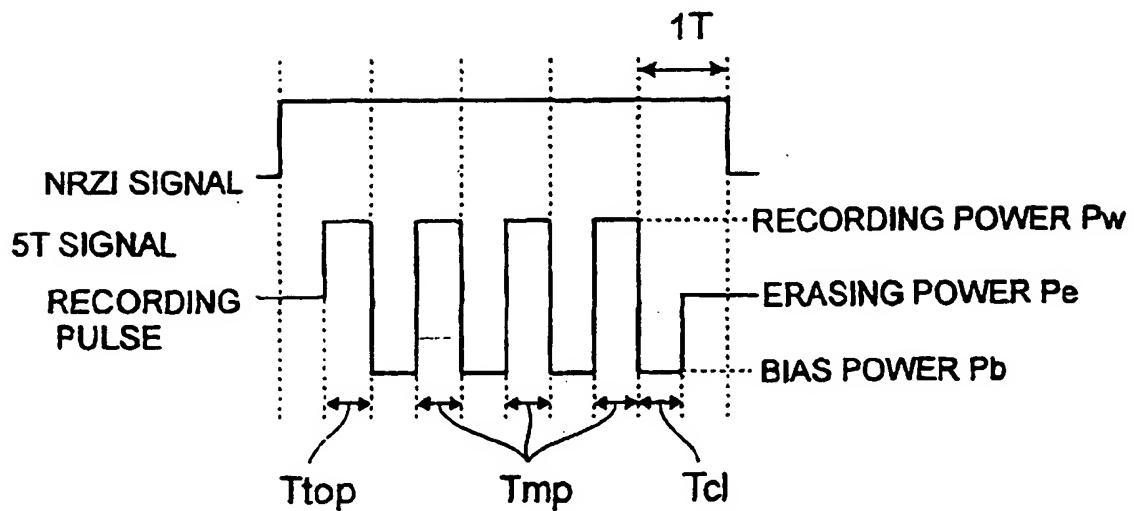
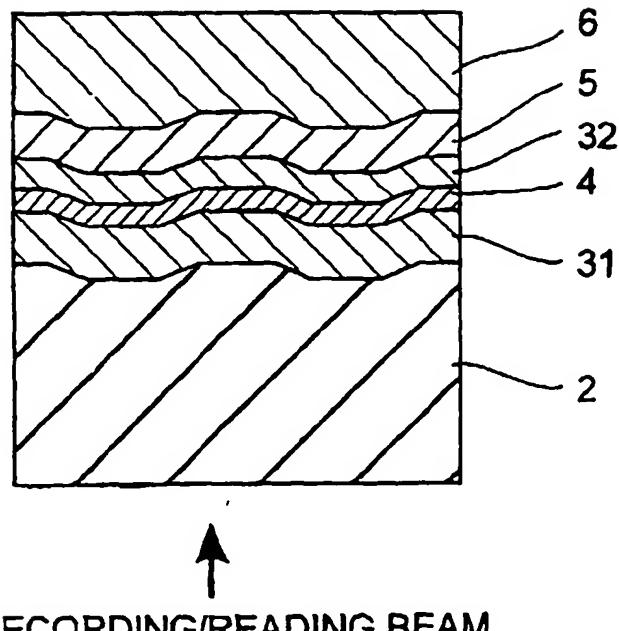


FIG. 4



**FIG. 5**



**FIG. 6**

RECORDING/READING BEAM

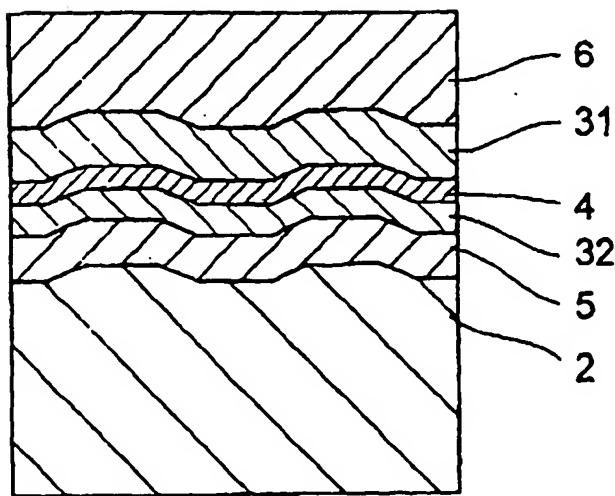


FIG. 7

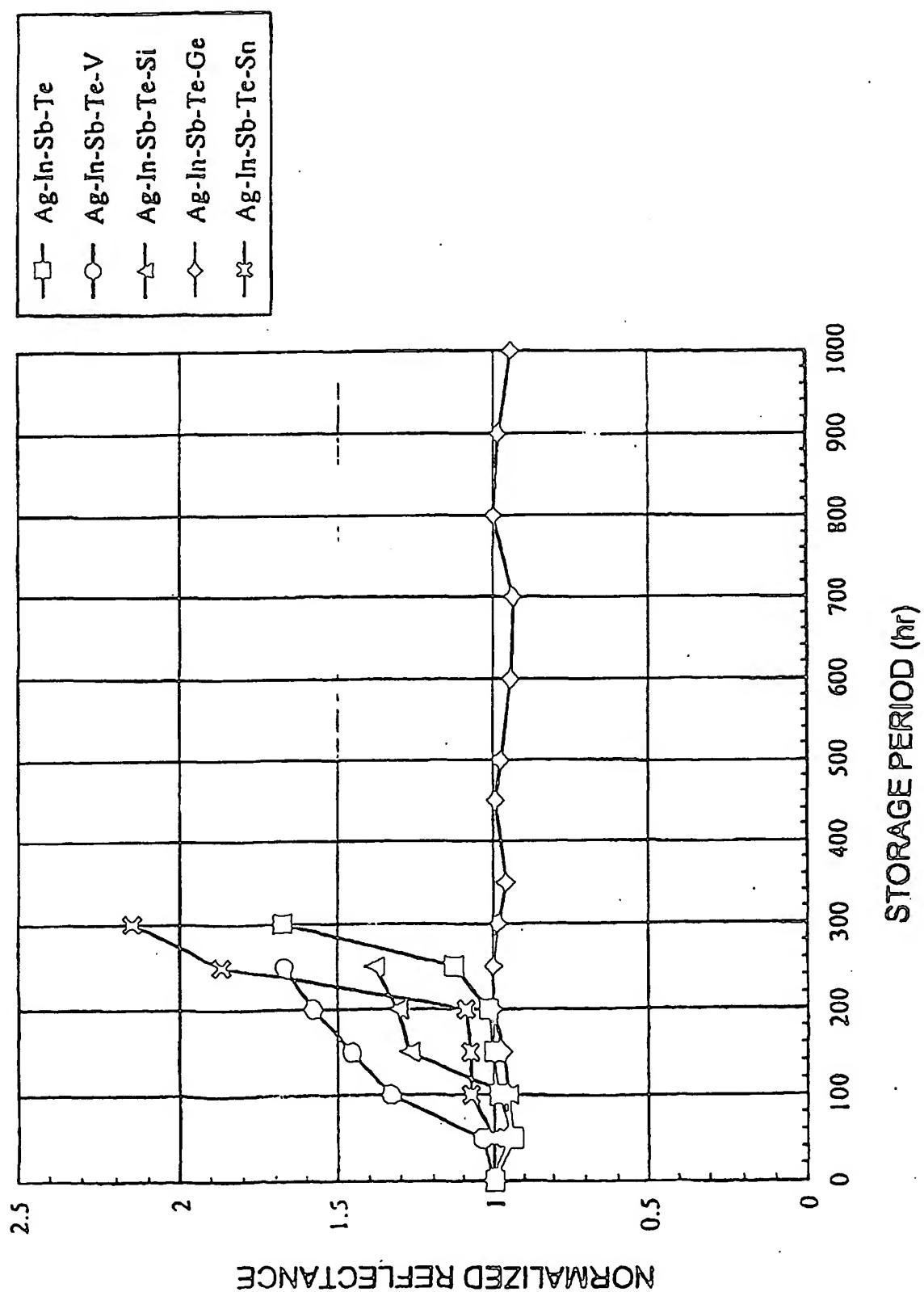


FIG. 8A

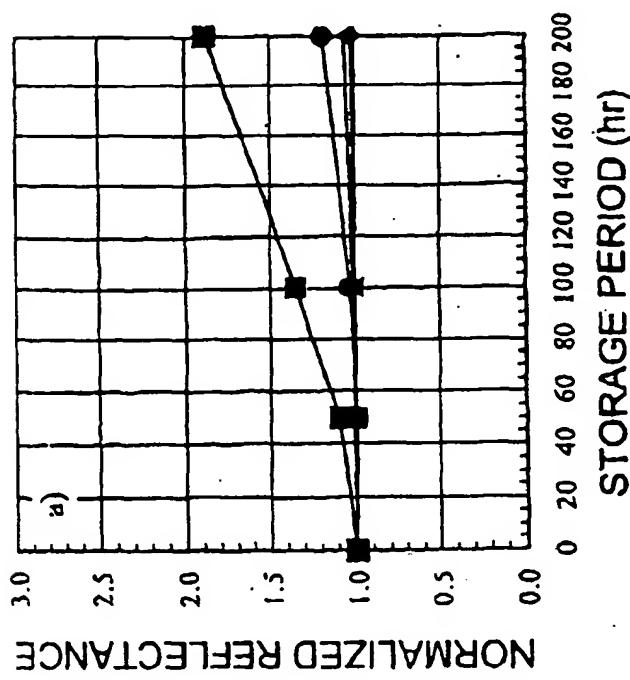
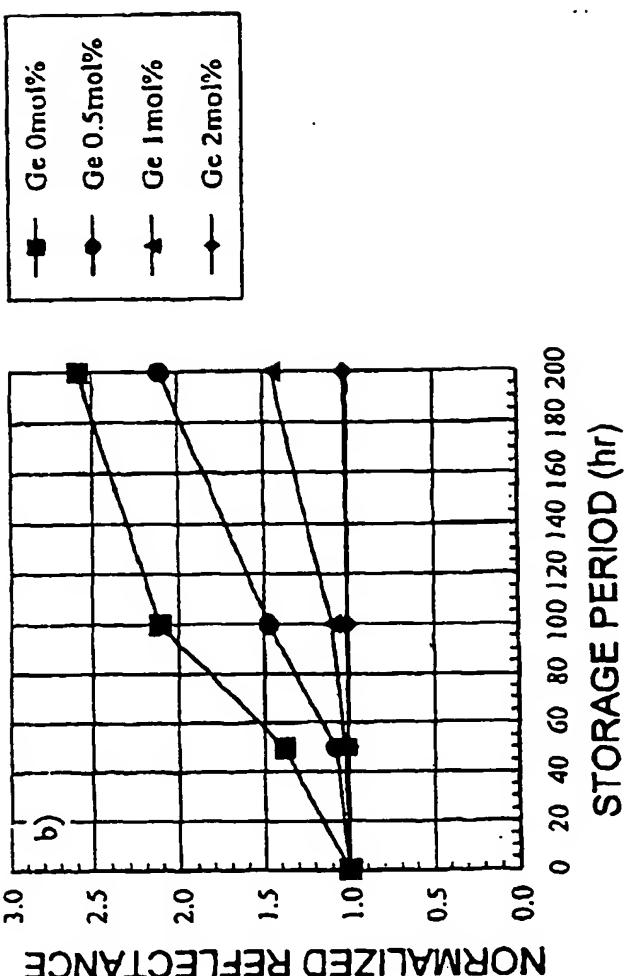
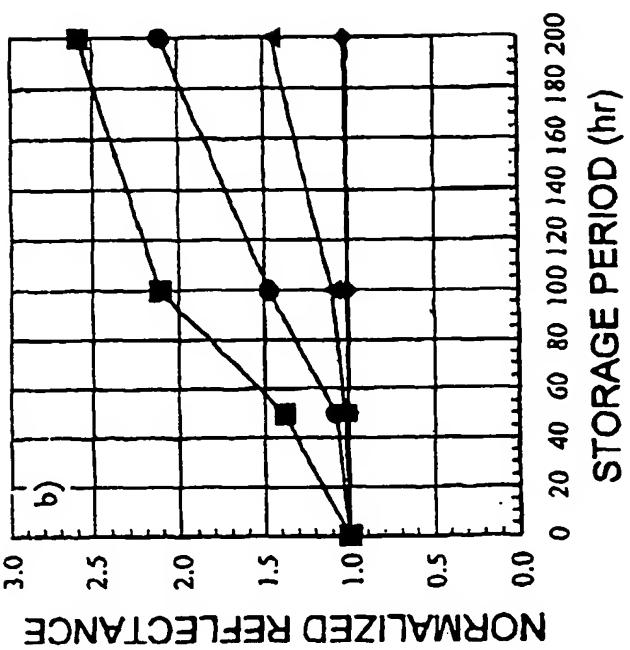


FIG. 8B





DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (IntCL7)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	EP 0 871 164 A (TDK CORP) 14 October 1998 (1998-10-14) * page 9, line 24 - page 10, line 28 *	1	G11B7/24 G11B7/013
Y	* page 12, line 31 - line 37 *	2	
Y	EP 0 867 868 A (MITSUBISHI CHEM CORP) 30 September 1998 (1998-09-30) * page 2, line 10 - line 22 * * page 13, line 32 - line 34; examples 1,8 *	2	
A		1	
X	EP 0 844 607 A (HITACHI LTD ;HITACHI MAXELL (JP)) 27 May 1998 (1998-05-27) * column 19, line 12 - line 49 *	1,2	
A	EP 0 717 404 A (RICOH KK) 19 June 1996 (1996-06-19) * abstract * * page 7, line 20 - line 58; example 23 *	1,2	TECHNICAL FIELDS SEARCHED (IntCL7)
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	30 March 2000	Annibal, P	
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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